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## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-310451

(43)Date of publication of application : 09.11.1999

(51)Int.Cl.

C04B 35/10  
H01L 21/205  
// H01L 21/3065

(21)Application number : 10-115241

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(22)Date of filing : 24.04.1998

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## (54) ALUMINA CERAMICS MATERIAL EXCELLENT IN PLASMA CORROSION RESISTANCE AND ITS PRODUCTION

## (57)Abstract:

PROBLEM TO BE SOLVED: To produce an alumina ceramics material having excellent corrosion resistance to a fluorine-based plasma.

SOLUTION: This alumina ceramics material comprises an alumina sintered compact having  $\geq 99.75\%$  alumina purity, 4-15  $\mu\text{m}$  average crystal grain diameter and  $\geq 3.94 \text{ g/cm}^3$  bulk density. Furthermore, the material has a surface having  $\geq 0.34$  crystal orientation ratio determined by the formula  $I_{030}/(I_{113}+I_{030})$  [I030 and I113 are each the intensity of the peaks corresponding to the alumina crystal {030} face and {113} face of a diffraction pattern obtained by an X-ray diffractometric measurement] in the X-ray diffractometric measurement as the surface having plasma corrosion resistance.

## LEGAL STATUS

[Date of request for examination] 01.08.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3555442

[Date of registration] 21.05.2004

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**CLAIMS**

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[Claim(s)]

[Claim 1] Alumina purity is 99.75% or more, and the diameter of average crystal grain is 4 micrometers - 15 micrometers, and bulk density is 3.94g/cm. It consists of alumina ceramics which they are above. And it sets to X diffraction measurement and is formula  $I_{030}/(I_{113}+I_{030})$  (among a formula).  $I_{030}$  And  $I_{113}$  the reinforcement of the peak corresponding to the alumina crystal {030} side of a diffraction pattern and {113} sides which are acquired by said X diffraction measurement, respectively -- it is -- The alumina-ceramics ingredient excellent in plasma corrosion resistance characterized by having the front face whose rate of crystal orientation called for is 0.34 or more as a front face of plasma corrosion resistance.

[Claim 2] The manufacture approach of an alumina-ceramics ingredient of having excelled in the plasma corrosion resistance characterized by having the process which performs pressing to 1 shaft orientations about the process which carries out temporary quenching of said alumina raw material powder at the temperature of 1000 degrees C - 1150 degrees C, and the ingredient which performed said temporary quenching before fabricating said alumina raw material powder in the approach of manufacturing an alumina-ceramics ingredient by sintering the Plastic solid which fabricated alumina raw material powder and was acquired.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the alumina-ceramics ingredient which has the corrosion resistance which was excellent especially to the fluorine system plasma exposure required for semi-conductor processes, such as etching, production of the semi-conductor epitaxial growth film, and manufacture of an LSI circuit, and its manufacture approach about alumina ceramics excellent in plasma corrosion resistance, and its manufacture approach.

[0002]

[Description of the Prior Art] The equipment which process using the plasma of a plasma etching system , a plasma ashing device , plasma CVD equipment , etc. can perform efficient required processing at low temperature , and it be indispensable from the point that control of processing also have few possibilities of it be comparatively easy and give a damage to ingredients , such as a semi-conductor substrate , in manufacture of high integrated semiconductor equipment , a liquid crystal display , etc.

[0003] Introduce reactant gas in the container which should perform processing decompressed near the vacuum, impress a RF and microwave, a discharge in gases is made to cause, and the plasma is made to generate with these equipments. Drawing 1 shows typically an example of this kind of plasma treatment equipment. In this equipment, it is laid on the sample base 23 and the surroundings of it are surrounded with a protective plate 24. And when plasma treatment is performed to the front face of the ingredient held by the clamper 25, the inside of the plasma production room 20 from the gas supply line 13 after performing exhaust air from an exhaust port 14 and setting the inside of the reaction container 11 as a predetermined degree of vacuum -- CF<sub>4</sub>, C three F<sub>8</sub>, Cl<sub>2</sub>, and HBr, Ar and O<sub>2</sub> etc. -- reactant gas is supplied. Cooling water is poured during actuation of equipment at the cooling water circulation room 18, and the circumference of the reaction container 11 is cooled. Microwave is introduced into the dielectric wire way 12 through a waveguide 15 from a microwave oscillator 16. Electric field are formed in dielectric wire way 12 lower part by this, and the formed electric field pass the microwave installation aperture 22, and are introduced in the plasma production room 20. The gas supplied from the gas supply line 13 is introduced in the plasma production room 20, and is plasma-ized by the exposure of microwave. Among plasma, a neutral radical mainly passes the mesh-like dashboard 17, and reaches on the front face of breadth and an ingredient in a reaction chamber 21 electrically, and plasma treatment is performed. Moreover, in such equipment, an electrostatic chuck etc. is used as a fixture holding the ingredient which should be carried out plasma treatment.

[0004] In such plasma treatment equipment, a microwave installation aperture, a protective plate, a clamper, an electrostatic chuck, etc. are exposed to the plasma. Therefore, these members need to have corrosion resistance to the plasma. A member which has the outstanding corrosion resistance is desired to the reactant higher fluorine system plasma especially generated from fluorocarbon and other fluorine content gas.

[0005] JP,8-81258,A indicates the technique for offering the alumina-ceramics sintered compact which

is excellent in dry etching-proof nature. As for an alumina-ceramics sintered compact, according to this official report, 99.99 or less % of the weight of an aluminum oxide and the remainder consist of an oxide of metals other than aluminum 99.2% of the weight or more, and mean particle diameter is 0.5 micrometers or more 1.5 micrometers or less in there, and consistencies are 3.88 g/cm<sup>3</sup>. It is 3.97 g/cm<sup>3</sup> above. It is the following. Moreover, this sintered compact that carried out the grinding process is heat-treated over 6 or less hours for 0.1 hours or more at 1000-degree-C or more temperature of 1550 degrees C or less.

[0006] JP,8-231266,A indicates the technique for offering the improved aluminum ceramic ingredient which has strong resistance to etching by the fluorine plasma. According to this official report, the improved alumina-ceramics ingredient consists of 99.5 % of the weight - 99.8% of the weight of an alumina, and binders, such as 0.5 % of the weight - 0.2% of the weight of a silica, and CaO, MgO, and it has the particle size distribution of the single mode centering on 15 micrometers - 30 micrometers.

[0007] JP,9-2864,A also indicates the technique for offering the alumina-ceramics ingredient which has high resistance to the fluorine plasma. According to this official report, a polycrystal alumina-ceramics ingredient forms the non-sintered compact which consists of 99.3 % of the weight - 99.7% of the weight of an alumina, and 0.7 % of the weight - 0.3% of the weight of a binder, and is manufactured by sintering at the temperature of about 1400 degrees C - 1700 degrees C for about 8 to 12 hours. At this time, area % of the non-sintered particle in a polycrystal alumina-ceramics ingredient does not exceed 0.1 area %.

[0008]

[Problem(s) to be Solved by the Invention] The alumina-ceramics member used for the equipment for a semi-conductor process etc. is expected to fulfill conditions, like that it is the thing of level which can disregard the contamination to workpieces, such as that damage does not progress locally by the plasma exposure other than having the corrosion resistance which was excellent to the plasma, especially the fluorine system plasma, and a wafer, that material strength is comparatively large, and it can manufacture by the suitable man day. With the alumina-ceramics ingredient indicated by JP,8-231266,A, alumina purity is comparatively low, and since elements, such as calcium and Mg, are included as a binder, possibility of being set to the level which cannot disregard the contamination to a wafer can be considered. Moreover, with this ingredient, since the particle-size consistency is comparatively large, the standard of typical reinforcement is comparatively as small as 40,000psi(s) (about 28kg/mm<sup>2</sup>). Moreover, since such an ingredient has the comparatively small sintered compact consistency, it is thought that damage tends (it can be easy to dig deeply) to progress locally by plasma exposure. Alumina purity is comparatively low, and since the ceramic ingredient indicated by JP,9-2864,A also contains elements, such as calcium and Mg, as BAIDA, it is considered may be set to the level which cannot disregard the contamination to a wafer. Moreover, it is thought that the manufacture process indicated by this official report has comparatively many routing counters, and it is not so good since sintering time amount is comparatively as long as 8 - 12 hours. [ of productive efficiency ] With the technique indicated by JP,8-81258,A, 0.1 - 6 hours needs to be heat-treated of 1000-1550 degrees C after sintering and a grinding process. It is necessary to look for proper conditions according to distortion, the amount of micro cracks, etc. which were generated at the time of sintering, and a production process becomes more complicated for such heat-treatment. Moreover, with this technique, the sintered compact consistency shown concretely does not become so high, but it is thought that there is room to raise an etching-proof property further.

[0009] The purpose of this invention is offering the outstanding alumina-ceramics ingredient of the corrosion resistance over a plasma exposure rather than the conventional ingredient.

[0010] The further purpose of this invention is offering the technique the corrosion resistance over the fluorine system plasma being excellent, and an alumina-ceramics ingredient with high reinforcement being manufactured according to a comparatively simple process.

[0011]

[Means for Solving the Problem] this invention person came to complete this invention by the corrosion resistance over the fluorine plasma of an alumina sintered compact finding out that it is dependent on

alumina purity, a sintered compact consistency, mean particle diameter, and a crystal stacking tendency, and setting up more desirable conditions about them.

[0012] Namely, the alumina-ceramics ingredient excellent in the plasma corrosion resistance by this invention Alumina purity is 99.75% or more, and the diameter of average crystal grain is 4 micrometers - 15 micrometers, and bulk density is 3.94 g/cm<sup>3</sup>. It consists of alumina ceramics which they are above. And it sets to X diffraction measurement and is formula  $I_{030}/(I_{113}+I_{030})$  (among a formula).  $I_{030}$  And  $I_{113}$  the reinforcement of the peak corresponding to the alumina crystal {030} side of a diffraction pattern and {113} sides which are acquired by X diffraction measurement, respectively -- it is -- The rate of crystal orientation called for is characterized by having the front face which is 0.34 or more as a front face of plasma corrosion resistance.

[0013] Moreover, the manufacture approach of an alumina-ceramics ingredient excellent in the plasma corrosion resistance by this invention is characterized by to have the process which performs pressing to 1 shaft orientations in the approach of manufacturing a ceramic ingredient by sintering the Plastic solid which fabricated alumina raw material powder and was acquired, about the process which carries out temporary quenching of the alumina raw material powder at the temperature of 1000 degrees C - 1150 degrees C before fabricating alumina raw material powder, and the ingredient which performed temporary quenching.

[0014] According to this invention which has the above description, the member by which the etch rate to a plasma exposure was stopped by 1/2 or less rather than the member by the conventional technique can be offered, for example.

[0015]

[Embodiment of the Invention] This invention is applicable to the component or components of equipment which are used for processes, such as production of for example, wafer etching, ashing, and the semi-conductor epitaxial growth film, CVD, LSI circuit manufacture, and liquid crystal display manufacture. More specifically, this invention can constitute vacuum chamber components, such as equipment wall material, shielding material, plate material, and clamp material, the dummy wafer for surface preparation, the hand for silicon wafers, a microwave installation aperture, an electrostatic chuck, etc. Hereafter, this invention is explained more concretely.

[0016] The corrosion of the ceramic material by plasma exposure advances the grain boundary between crystal grain, and within crystal grain. In order to raise the corrosion resistance of a ceramic ingredient, it is important to lose reduction and the opening of the impurity layer in which the corrosion resistance which exists in a grain boundary is inferior, and to raise [ both ] the corrosion resistance of the crystal grain itself.

[0017] First, by raising the alumina purity in alumina ceramics, the impurity contained in a sintered compact can be reduced and the generation and the deposit of an impurity layer in a grain boundary can be controlled. In this invention, an ingredient with little corrosion by the plasma in a grain boundary is offered by making alumina purity into 99.75% or more. If this purity is less than 99.75%, it will become difficult to give more desirable corrosion resistance to a ceramic ingredient.

[0018] Moreover, the opening part which exists in a grain boundary can be decreased by what the bulk density of a Plastic solid is raised for (eburnation is carried out), and the corrosion resistance over the plasma can be raised. At this invention, it is the bulk density of a ceramic ingredient 3.94 g/cm<sup>3</sup> Plasma corrosion resistance is raised by considering as the above. If this bulk density is less than 3.94 g/cm<sup>3</sup>, more desirable corrosion resistance will no longer be acquired, and also the reinforcement of an ingredient becomes low relatively.

[0019] Furthermore, the rate (area) that a part with low (grain boundary) plasma resistance occupies to a plasma exposure side can be reduced by enlarging mean particle diameter of the alumina crystal grain which carried out eburnation in the predetermined range (that is, a grain boundary consistency can be decreased). In this invention, mean particle diameter of alumina crystal grain is set to 4 micrometers or more 15 micrometers or less. If the mean particle diameter of alumina crystal grain increases, a grain boundary consistency will decrease, but since the anti-chip box reinforcement of a member falls gradually, the mean particle diameter has desirable 15 micrometers or less. Moreover, when the mean

particle diameter is less than 4 micrometers, a grain boundary consistency cannot fully be decreased and the degree of the plasma damage in a grain boundary becomes large.

[0020] Furthermore, this invention person found out depending for the amount of etching by the plasma of the alumina crystal grain itself to the crystal stacking tendency of the plasma exposure side in a ceramic ingredient strongly. And as a result of research, when many alumina crystal (h00) sides and (0k0) fields on the plasma exposure front face of a ceramic ingredient were distributed, it became clear that this front face was excellent in etching-proof nature. Drawing 2 supports such a result concretely and shows the correlation of the crystal stacking tendency of a member, and an etch rate. In drawing 1, an axis of ordinate shows the rate of crystal orientation in the front face of an alumina-ceramics ingredient ( $I_{030}/(I_{113}+I_{030})$ ), and an axis of abscissa shows the rate (micrometer/hour) into which this front face is etched by the plasma. As the rate of crystal orientation becomes high, it is clearer than drawing 1 that the plasma becomes an etch rate falls, namely, is hard to be etched. A field (h00) and (0k0) a field mean that this is high corrosion resistance to a plasma exposure in each crystal face of an alumina. Therefore, it becomes possible to raise plasma corrosion resistance by carrying out many orientation of a field (h00) and (0k0) the field on the front face of alumina-ceramics material.

[0021] Here, the rate of crystal orientation is called for by X diffraction measurement on the front face of an ingredient. If an ingredient front face is measured  $2\theta/\theta$  using the usual X-ray diffractometer by law (general approach used for identification of the crystal structure of bulk material and a powder ingredient), a diffraction pattern as shown, for example in drawing 3 will be obtained. In this pattern, reinforcement is obtained about the peak originating in the {113} sides of alumina crystal system, and {030} sides. Generally, reinforcement is obtained as height of a peak. And obtained reinforcement  $I_{030}$  And  $I_{113}$  The rate of crystal orientation is called for according to formula  $I_{030}/(I_{113}+I_{030})$ . In addition, generally, it is hexagonal and the crystal structure of a stable alumina of an a-axis and a b-axis is equivalent among three crystallographics axis as shown in drawing 4. Therefore, in the case of such hexagonal structure, the field (030) and the field (300) are equivalent, are named generically and made into {030} sides.

[0022] Drawing 5 shows typically signs that {030} sides carry out orientation to the front face, in the alumina-ceramics ingredient by this invention. The ingredient shown in drawing 5 has the configuration of a rectangular parallelepiped. Such an ingredient has one pair of principal planes (a top face and base), and the side face which exists between them. According to this invention, in such an ingredient, orientation of the {030} sides can be strongly carried out almost in parallel to one pair of principal planes (a top face and base), and the rate of crystal orientation mentioned above in these fields can be made or more into 0.34. These front faces whose rates of orientation are 0.34 or more have the more excellent plasma corrosion resistance, and have the engine performance which was excellent as a plasma exposure side. On the other hand, in such a case, {030} sides have not carried out orientation to a side face strongly. However, the side face in which the conditions of alumina purity, a sintered compact consistency, and mean particle diameter are satisfied as mentioned above also has plasma corrosion resistance. The more excellent plasma corrosion resistance was able to be given by making the rate of crystal orientation on the front face of an ingredient or more into 0.34 so that the example shown below might show more concretely.

[0023] The front face which was excellent with such plasma corrosion resistance can be obtained in the manufacture process of the ceramics including shaping of powder and the process of sintering by carrying out temporary quenching of the alumina raw material powder at 1000 degrees C - 1150 degrees C, and carrying out pressing to 1 shaft orientations about the raw material which performed such temporary quenching treatment. According to a 1000 degrees C - 1150 degrees C [ such ] temporary-quenching process, alumina powder turns into raw material powder to which it has an anisotropy about a configuration, and particle size was equal (that is, the raw material with which neck growth took place is obtained). It is desirable to use the alumina powder of a high grade to which particle size was equal in what has comparatively small mean particle diameter (for example, mean particle diameter of 0.3-0.5 micrometers) for the raw material powder for presenting such a temporary-quenching process. Such alumina powder can be obtained as a commercial item. As mentioned above, after carrying out



temporary quenching of the alumina powder, the orientation of the {030} sides can be made to carry out in the direction almost perpendicular to these 1 shaft orientations strongly by pressing into 1 shaft orientations. Here, the compression moulding technique to which a load is applied only in the direction parallel to one certain shaft as the pressing of 1 shaft orientations as shown in drawing 6 is meant. The rate of crystal orientation can use the field where the pressure was put on 1 shaft orientations in the Plastic solid acquired after these processes as 0.34 or more front faces. The alumina ceramics according to this invention can be manufactured by performing CIP shaping after such a press of 1 shaft orientations, and subsequently sintering. On the other hand, after the pressing of 1 shaft orientations, even if it sinters without performing CIP shaping, an ingredient with the high crystal stacking tendency on the front face of a sintered compact can be obtained.

[0024] Except surely performing the temporary-quenching process mentioned above and the pressing process of 1 shaft orientations, the manufacture approach by this invention can follow the usual conditions. That is, in a general process, as the alumina powder (generally powder of stable alpha mold (corundum structure) alumina) of a high grade was mentioned above, after carrying out temporary quenching, an organic binder, a dispersant, water, etc. are added to the raw material powder obtained, and a slurry is prepared. If needed, a spray dryer etc. is used, the obtained slurry is corned and dried, and the end of agglomerated powder is obtained. Thus, as the end of agglomerated powder it was obtained is put into metal mold and mentioned above, after carrying out pressing to 1 shaft orientations, CIP shaping is performed if needed. Thus, after heating the acquired Plastic solid and degreasing, sintering is performed and the alumina ceramics which have a required configuration according to an application are obtained. Sintering temperature can be made into 1550 degrees C - 1720 degrees C. Thus, about the obtained alumina-ceramics material, required processing of a grinding process, polish processing, etc. is performed, and a product is obtained through a suitable washing process etc. The obtained product can be offered as the component or components of the equipment used for a semi-conductor process which was mentioned above, for example.

[0025]

[Example] Example mean particle diameter is 0.5 micrometers, while being 99.8% - 99.99%, temporary quenching of the alumina raw material powder which has various purity was carried out at 1000-1150 degrees C for 1 to 2 hours, and neck growth was made to perform. Thus, in the raw material powder 100 weight section which carried out temporary quenching, the water 60 weight section, the ammonium system dispersant 0.3 weight section, and the polyvinyl alcohol system binder 2 weight section were added, and the slurry was obtained by mixing with a ball mill for 16 hours. The agglomerated powder of spherical granulation was prepared by carrying out spray drying of the obtained slurry with a spray dryer. The obtained agglomerated powder is set to metal mold, and it is 300kg/cm<sup>2</sup> to 1 shaft orientations. Pressing was carried out by the pressure. To the acquired Plastic solid, it sets further at a rubber die, and is 2 1.2t/cm. CIP shaping was given by the pressure. It degreased by having carried out the temperature up of the acquired Plastic solid in the small electric furnace, it calcinated at 1550-1720 degrees C for 2 hours, and alumina ceramics were obtained. Thus, the front face of the obtained alumina ceramics was wrapped with the precision grinder, using a diamond slurry with a mean particle diameter of 0.5-1.0 micrometers as abrasives, and the member front face was mirror-plane-ized.

[0026] About the obtained alumina-ceramics ingredient, bulk density, alumina purity, the diameter of average crystal grain, the rate of crystal orientation, the etch rate by plasma exposure, and anti-chip box reinforcement were measured. Bulk density was measured by the Archimedes method. Alumina purity was measured by ICP emission spectrometry. The diameter of average crystal grain was measured by photo finish by SEM observation. a crystal -- orientation -- a rate -- measurement -- \*\*\*\* -- GONIO -- a formula -- X-ray diffractometer -- using -- each -- an alumina -- an ingredient (10mmx10mm) -- main -- a front face -- receiving -- an X diffraction -- an image -- observing -- an angle of diffraction -- whenever -- 43.36 -- degree -- 68.19 -- degree -- respectively -- appearing -- {-- 113 --} -- a field -- {-- 030 --} -- a field -- a peak -- diffraction -- reinforcement -- from -- a formula --  $I_{030} / (I_{113} + I_{030})$  -- the rate of crystal orientation -- having asked . In the plasma exposure to a ceramic ingredient, the plasma exposure was carried out on the conditions shown in Table 1 using parallel monotonous mold

ion etching equipment. The mask on a Teflon tape was partially prepared in the exposure side (polished surface mentioned above) of each trial ingredient, and the plasma exposure was performed. The Teflon tape after an exposure was removed, and the amount of corrosion in a plasma exposure side (the amount of damages) was calculated on the basis of the non-irradiating field (plasma non-irradiated side) by which the mask was carried out, and it asked for the total etch rate. This amount of damages was calculated from both level difference measurement with the exposure side and the non-irradiating field by the sensing-pin type level difference meter, and measurement of the amount of surface irregularity by the atomic force microscope (AFM). That is, as shown in drawing 7 , the amount of surface irregularity shown by A was calculated by AFM, and the amount of level differences shown by B was calculated with the sensing-pin type level difference meter. The amount of damages by the plasma totals these amounts. Moreover, it asked for the anti-chip box reinforcement of each trial ingredient by the three-point bending test.

[0027]

[Table 1]

照射条件

高周波周波数	13.56 MHz
高周波出力	0.8 kW
電極間距離	~ 20 cm
エッチングガス種	CF <sub>4</sub>
雰囲気圧力	5 Pa
照射時間	3 時間

[0028] The example mean particle diameter of a comparison is 0.5 micrometers, while being 99.3% - 99.99%, about the examples 1-4 of a comparison, temporary quenching of the alumina raw material powder which has various purity was carried out at 1020-1210 degrees C for 1 to 2 hours, and neck growth was made to perform. Thus, in the raw material powder 100 weight section which carried out temporary quenching, the water 60 weight section, the ammonium system dispersant 0.3 weight section, and the polyvinyl alcohol system binder 2 weight section were added, and the slurry was obtained by mixing with a ball mill for 16 hours. The agglomerated powder of spherical granulation was prepared by carrying out spray drying of the obtained slurry with a spray dryer. the obtained agglomerated powder -- metal mold -- it is -- 1 shaft orientations -- 300kg/cm<sup>2</sup> Pressing was carried out by the pressure. It sets further to the acquired Plastic solid at a rubber die, and they are 1.2 t/cm<sup>2</sup>. CIP shaping was carried out by the pressure. After degreasing by carrying out the temperature up of the acquired Plastic solid using a small electric furnace, it calcinated at the temperature of 1510-1770 degrees C for 2 hours. After performing polish processing like [ alumina ceramics / which were obtained ] the above-mentioned example and mirror-plane-izing a front face, it asked for bulk density, purity, a mean diameter, the rate of crystal orientation, an etch rate, and anti-chip box reinforcement like the above-mentioned example.

[0029] Moreover, about the example 5 of a comparison, temporary quenching of the alumina raw material powder was not carried out, but, as for the pressing of 1 shaft orientations, agglomerated powder also performed CIP shaping, without carrying out. Other conditions were the examples 1-4 of a comparison, and these conditions.

[0030] The result obtained in the example and the example of a comparison, respectively is shown [ example / temperature / burning temperature and / temporary-quenching ] in Table 2 and 3 with burning temperature about the example of a comparison. It is the bulk density of alumina ceramics so that clearly [ compare these results and ] 3.94 g/cm<sup>3</sup> By making mean particle diameter to 4 micrometers - 15 micrometers, making alumina purity into 99.75% or more, and making the rate of crystal orientation of the front face or more into 0.34 shows above that the ingredient which is excellent in the corrosion resistance over the fluorine system plasma, and has high anti-chip box reinforcement is



obtained. Moreover, in order to make the rate of crystal orientation on the front face of a sintered compact increase, a temporary-quenching process (neck growth process) is indispensable, and it turns out that the rate of crystal orientation on the front face of an ingredient increases with the rise of temporary-quenching temperature. In addition, in this invention, desirable temporary-quenching temperature is 1000-1150 degrees C, if this temporary-quenching temperature is less than 1000 degrees C, neck growth of alumina powder will not fully advance, and if temporary-quenching temperature exceeds 1150 degrees C, the diameter of granulation will become large, therefore pack density falls and the bulk density of the sintered compact obtained becomes small. In the alumina ceramic material by this invention, an etch rate is small in 0.5micrometers/[ an hour and ] or less so that clearly [ compare an ingredient (comparison material 1) with low bulk density, an ingredient with low purity (comparison material 2), an ingredient (comparison material 3) with a small particle size, an ingredient (comparison material 4) with a big particle size, and an ingredient with the low rate of crystal orientation (comparison material 5) with the ingredient obtained in the example and ], and anti-chip box reinforcement is 35kg/cm<sup>2</sup>. It turns out [ the above and ] that it is large. Moreover, signs that the ingredient of an example and the ingredient (comparison material 2) of the example of a comparison whose sintering temperature is 1670 degrees C were compared about the etch rate are shown in drawing 8 . With the ingredient by this invention, it is fewer than comparison material about all of the amount of etching by the level difference shown by the amount of etching and B by the irregularity shown by A, and it turns out that it has the corrosion resistance in which the ingredient by this invention was excellent to the fluorine system plasma so that clearly from drawing.

[0031]

[Table 2]

	焼成温度 (°C)	仮焼温度 (°C)	密度 (g/cm <sup>3</sup> )	純度 (%)	平均粒径 (μm)	結晶配向率	エッチング速度 (μm/hr)	抗析強度 (kg/mm <sup>2</sup> )
実施例	1550	1000	3.940	99.8	3.8	0.34	0.50	47
	1550	1150	3.942	99.8	4.8	0.36	0.47	43
	1610	1020	3.946	99.8	4.9	0.35	0.42	42
	1610	1110	3.948	99.8	4.7	0.37	0.40	45
	1630	1040	3.956	99.99	6.2	0.36	0.38	38
	1630	1150	3.954	99.99	6.8	0.39	0.33	40
	1650	1020	3.961	99.87	7.5	0.35	0.35	39
	1650	1100	3.963	99.87	7.2	0.38	0.33	40
	1650	1150	3.959	99.87	6.6	0.40	0.31	43
	1670	1100	3.964	99.91	8.2	0.38	0.35	35
	1670	1140	3.967	99.91	7.9	0.41	0.33	42
	1709	1040	3.969	99.85	12	0.41	0.32	33
	1709	1150	3.970	99.85	10	0.43	0.28	36
	1730	1030	3.975	99.99	14	0.41	0.2	32

[0032]

[Table 3]

		焼成温度 (°C)	仮焼温度 (°C)	密度 (g/cm <sup>3</sup> )	純度 (%)	平均粒径 (μm)	結晶配向率	エッチング速度 (μm/hr)	抗析強度 (kg/mm <sup>2</sup> )
比較例	1	1540	1210	3.915	99.92	4.2	0.35	0.87	43
		1550	1170	3.930	99.95	4.5	0.37	0.92	41
		1570	1180	3.935	99.8	4.6	0.37	0.80	46
	2	1650	1100	3.956	99.55	7.3	0.38	0.70	38
		1670	1080	3.962	99.3	8.5	0.37	1.20	32
	3	1510	1020	3.955	99.93	3.0	0.34	0.96	32
		1520	1050	3.950	99.92	3.2	0.35	0.88	39
	4	1750	1100	3.961	99.93	18	0.36	0.42	16
		1770	1120	3.971	99.99	21	0.39	0.38	12
	5	1630	—	3.956	99.99	7.2	0.28	0.78	38
		1650	—	3.961	99.87	7.6	0.29	0.65	41
		1670	—	3.964	99.91	10.2	0.31	0.55	40

[0033]

[Effect of the Invention] According to this invention, the corrosion resistance over the plasma, especially the fluorine system plasma is more excellent, and an alumina-ceramics ingredient with high reinforcement can be obtained as explained above. Formation of etching, ashing, and the semi-conductor epitaxial growth film, manufacture of an LSI circuit, the manufacture of a liquid crystal display of this invention, etc. are useful especially as the component or components of the equipment used for a semi-conductor process. Moreover, the alumina-ceramics ingredient which has a front face superior to corrosion resistance one to the plasma can be obtained by combining a temporary-quenching process and the pressing process of 1 shaft orientations, as mentioned above. Especially, such a manufacture approach does not need a complicated process and can perform it by the suitable man day.

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PRIOR ART

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[Description of the Prior Art] The equipment which process using the plasma of a plasma etching system, a plasma ashing device, plasma CVD equipment, etc. can perform efficient required processing at low temperature, and it be indispensable from the point that control of processing also have few possibilities of it be comparatively easy and give a damage to ingredients, such as a semiconductor substrate, in manufacture of high integrated semiconductor equipment, a liquid crystal display, etc.

[0003] Introduce reactant gas in the container which should perform processing decompressed near the vacuum, impress a RF and microwave, a discharge in gases is made to cause, and the plasma is made to generate with these equipments. Drawing 1 shows typically an example of this kind of plasma treatment equipment. In this equipment, it is laid on the sample base 23 and the surroundings of it are surrounded with a protective plate 24. And when plasma treatment is performed to the front face of the ingredient held by the clamper 25, the inside of the plasma production room 20 from the gas supply line 13 after performing exhaust air from an exhaust port 14 and setting the inside of the reaction container 11 as a predetermined degree of vacuum -- CF<sub>4</sub>, C three F<sub>8</sub>, Cl<sub>2</sub>, and HBr, Ar and O<sub>2</sub> etc. -- reactant gas is supplied. Cooling water is poured during actuation of equipment at the cooling water circulation room 18, and the circumference of the reaction container 11 is cooled. Microwave is introduced into the dielectric wire way 12 through a waveguide 15 from a microwave oscillator 16. Electric field are formed in dielectric wire way 12 lower part by this, and the formed electric field pass the microwave installation aperture 22, and are introduced in the plasma production room 20. The gas supplied from the gas supply line 13 is introduced in the plasma production room 20, and is plasma-ized by the exposure of microwave. Among plasma, a neutral radical mainly passes the mesh-like dashboard 17, and reaches on the front face of breadth and an ingredient in a reaction chamber 21 electrically, and plasma treatment is performed. Moreover, in such equipment, an electrostatic chuck etc. is used as a fixture holding the ingredient which should be carried out plasma treatment.

[0004] In such plasma treatment equipment, a microwave installation aperture, a protective plate, a clamper, an electrostatic chuck, etc. are exposed to the plasma. Therefore, these members need to have corrosion resistance to the plasma. A member which has the outstanding corrosion resistance is desired to the reactant higher fluorine system plasma especially generated from fluorocarbon and other fluorine content gas.

[0005] JP,8-81258,A indicates the technique for offering the alumina-ceramics sintered compact which is excellent in dry etching-proof nature. As for an alumina-ceramics sintered compact, according to this official report, 99.99 or less % of the weight of an aluminum oxide and the remainder consist of an oxide of metals other than aluminum 99.2% of the weight or more, and mean particle diameter is 0.5 micrometers or more 1.5 micrometers or less in there, and consistencies are 3.88 g/cm<sup>3</sup>. It is 3.97 g/cm<sup>3</sup> above. It is the following. Moreover, this sintered compact that carried out the grinding process is heat-treated over 6 or less hours for 0.1 hours or more at 1000-degree-C or more temperature of 1550 degrees C or less.

[0006] JP,8-231266,A indicates the technique for offering the improved aluminum ceramic ingredient

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the alumina-ceramics ingredient which has the corrosion resistance which was excellent especially to the fluorine system plasma exposure required for semi-conductor processes, such as etching, production of the semi-conductor epitaxial growth film, and manufacture of an LSI circuit, and its manufacture approach about alumina ceramics excellent in plasma corrosion resistance, and its manufacture approach.

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[Translation done.]

which has strong resistance to etching by the fluorine plasma. According to this official report, the improved alumina-ceramics ingredient consists of 99.5 % of the weight - 99.8% of the weight of an alumina, and binders, such as 0.5 % of the weight - 0.2% of the weight of a silica, and CaO, MgO, and it has the particle size distribution of the single mode centering on 15 micrometers - 30 micrometers.

[0007] JP,9-2864,A also indicates the technique for offering the alumina-ceramics ingredient which has high resistance to the fluorine plasma. According to this official report, a polycrystal alumina-ceramics ingredient forms the non-sintered compact which consists of 99.3 % of the weight - 99.7% of the weight of an alumina, and 0.7 % of the weight - 0.3% of the weight of a binder, and is manufactured by sintering at the temperature of about 1400 degrees C - 1700 degrees C for about 8 to 12 hours. At this time, area % of the non-sintered particle in a polycrystal alumina-ceramics ingredient does not exceed 0.1 area %.

[0008]

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EFFECT OF THE INVENTION

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[Effect of the Invention] According to this invention, the corrosion resistance over the plasma, especially the fluorine system plasma is more excellent, and an alumina-ceramics ingredient with high reinforcement can be obtained as explained above. Formation of etching, ashing, and the semi-conductor epitaxial growth film, manufacture of an LSI circuit, the manufacture of a liquid crystal display of this invention, etc. are useful especially as the component or components of the equipment used for a semi-conductor process. Moreover, the alumina-ceramics ingredient which has a front face superior to corrosion resistance one to the plasma can be obtained by combining a temporary-quenching process and the pressing process of 1 shaft orientations, as mentioned above. Especially, such a manufacture approach does not need a complicated process and can perform it by the suitable man day.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The alumina-ceramics member used for the equipment for a semi-conductor process etc. is expected to fulfill conditions, like that it is the thing of level which can disregard the contamination to workpieces, such as that damage does not progress locally by the plasma exposure other than having the corrosion resistance which was excellent to the plasma, especially the fluorine system plasma, and a wafer, that material strength is comparatively large, and it can manufacture by the suitable man day. With the alumina-ceramics ingredient indicated by JP,8-231266,A, alumina purity is comparatively low, and since elements, such as calcium and Mg, are included as a binder, possibility of being set to the level which cannot disregard the contamination to a wafer can be considered. Moreover, with this ingredient, since the particle-size consistency is comparatively large, the standard of typical reinforcement is comparatively as small as 40,000psi(s) (about 28kg/mm<sup>2</sup>). Moreover, since such an ingredient has the comparatively small sintered compact consistency, it is thought that damage tends (it can be easy to dig deeply) to progress locally by plasma exposure. Alumina purity is comparatively low, and since the ceramic ingredient indicated by JP,9-2864,A also contains elements, such as calcium and Mg, as BAIDA, it is considered may be set to the level which cannot disregard the contamination to a wafer. Moreover, it is thought that the manufacture process indicated by this official report has comparatively many routing counters, and it is not so good since sintering time amount is comparatively as long as 8 - 12 hours. [ of productive efficiency ] With the technique indicated by JP,8-81258,A, 0.1 - 6 hours needs to be heat-treated of 1000-1550 degrees C after sintering and a grinding process. It is necessary to look for proper conditions according to distortion, the amount of micro cracks, etc. which were generated at the time of sintering, and a production process becomes more complicated for such heat-treatment. Moreover, with this technique, the sintered compact consistency shown concretely does not become so high, but it is thought that there is room to raise an etching-proof property further.

[0009] The purpose of this invention is offering the outstanding alumina-ceramics ingredient of the corrosion resistance over a plasma exposure rather than the conventional ingredient.

[0010] The further purpose of this invention is offering the technique the corrosion resistance over the fluorine system plasma being excellent, and an alumina-ceramics ingredient with high reinforcement being manufactured according to a comparatively simple process.

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MEANS

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[Means for Solving the Problem] this invention person came to complete this invention by the corrosion resistance over the fluorine plasma of an alumina sintered compact finding out that it is dependent on alumina purity, a sintered compact consistency, mean particle diameter, and a crystal stacking tendency, and setting up more desirable conditions about them.

[0012] Namely, the alumina-ceramics ingredient excellent in the plasma corrosion resistance by this invention Alumina purity is 99.75% or more, and the diameter of average crystal grain is 4 micrometers - 15 micrometers, and bulk density is 3.94g/cm. It consists of alumina ceramics which they are above. And it sets to X diffraction measurement and is formula  $I_{030}/(I_{113}+I_{030})$  (among a formula).  $I_{030}$  And  $I_{113}$  the reinforcement of the peak corresponding to the alumina crystal {030} side of a diffraction pattern and {113} sides which are acquired by X diffraction measurement, respectively -- it is -- The rate of crystal orientation called for is characterized by having the front face which is 0.34 or more as a front face of plasma corrosion resistance.

[0013] Moreover, the manufacture approach of an alumina-ceramics ingredient excellent in the plasma corrosion resistance by this invention is characterized by to have the process which performs pressing to 1 shaft orientations in the approach of manufacturing a ceramic ingredient by sintering the Plastic solid which fabricated alumina raw material powder and was acquired, about the process which carries out temporary quenching of the alumina raw material powder at the temperature of 1000 degrees C - 1150 degrees C before fabricating alumina raw material powder, and the ingredient which performed temporary quenching.

[0014] According to this invention which has the above description, the member by which the etch rate to a plasma exposure was stopped by 1/2 or less rather than the member by the conventional technique can be offered, for example.

[0015]

[Embodiment of the Invention] This invention is applicable to the component or components of equipment which are used for processes, such as production of for example, wafer etching, ashing, and the semi-conductor epitaxial growth film, CVD, LSI circuit manufacture, and liquid crystal display manufacture. More specifically, this invention can constitute vacuum chamber components, such as equipment wall material, shielding material, plate material, and clamp material, the dummy wafer for surface preparation, the hand for silicon wafers, a microwave installation aperture, an electrostatic chuck, etc. Hereafter, this invention is explained more concretely.

[0016] The corrosion of the ceramic material by plasma exposure advances the grain boundary between crystal grain, and within crystal grain. In order to raise the corrosion resistance of a ceramic ingredient, it is important to lose reduction and the opening of the impurity layer in which the corrosion resistance which exists in a grain boundary is inferior, and to raise [ both ] the corrosion resistance of the crystal grain itself.

[0017] First, by raising the alumina purity in alumina ceramics, the impurity contained in a sintered compact can be reduced and the generation and the deposit of an impurity layer in a grain boundary can be controlled. In this invention, an ingredient with little corrosion by the plasma in a grain boundary is

offered by making alumina purity into 99.75% or more. If this purity is less than 99.75%, it will become difficult to give more desirable corrosion resistance to a ceramic ingredient.

[0018] Moreover, the opening part which exists in a grain boundary can be decreased by what the bulk density of a Plastic solid is raised for (eburnation is carried out), and the corrosion resistance over the plasma can be raised. At this invention, it is the bulk density of a ceramic ingredient 3.94 g/cm<sup>3</sup> Plasma corrosion resistance is raised by considering as the above. If this bulk density is less than 3.94 g/cm<sup>3</sup>, more desirable corrosion resistance will no longer be acquired, and also the reinforcement of an ingredient becomes low relatively.

[0019] Furthermore, the rate (area) that a part with low (grain boundary) plasma resistance occupies to a plasma exposure side can be reduced by enlarging mean particle diameter of the alumina crystal grain which carried out eburnation in the predetermined range (that is, a grain boundary consistency can be decreased). In this invention, mean particle diameter of alumina crystal grain is set to 4 micrometers or more 15 micrometers or less. If the mean particle diameter of alumina crystal grain increases, a grain boundary consistency will decrease, but since the anti-chip box reinforcement of a member falls gradually, the mean particle diameter has desirable 15 micrometers or less. Moreover, when the mean particle diameter is less than 4 micrometers, a grain boundary consistency cannot fully be decreased and the degree of the plasma damage in a grain boundary becomes large.

[0020] Furthermore, this invention person found out depending for the amount of etching by the plasma of the alumina crystal grain itself to the crystal stacking tendency of the plasma exposure side in a ceramic ingredient strongly. And as a result of research, when many alumina crystal (h00) sides and (0k0) fields on the plasma exposure front face of a ceramic ingredient were distributed, it became clear that this front face was excellent in etching-proof nature. Drawing 2 supports such a result concretely and shows the correlation of the crystal stacking tendency of a member, and an etch rate. In drawing 1, an axis of ordinate shows the rate of crystal orientation in the front face of an alumina-ceramics ingredient (I030/(I113+I030)), and an axis of abscissa shows the rate (micrometer/hour) into which this front face is etched by the plasma. As the rate of crystal orientation becomes high, it is clearer than drawing 1 that the plasma becomes an etch rate falls, namely, is hard to be etched. A field (h00) and (0k0) a field mean that this is high corrosion resistance to a plasma exposure in each crystal face of an alumina. Therefore, it becomes possible to raise plasma corrosion resistance by carrying out many orientation of a field (h00) and (0k0) the field on the front face of alumina-ceramics material.

[0021] Here, the rate of crystal orientation is called for by X diffraction measurement on the front face of an ingredient. If an ingredient front face is measured 2 theta/theta using the usual X-ray diffractometer by law (general approach used for identification of the crystal structure of bulk material and a powder ingredient), a diffraction pattern as shown, for example in drawing 3 will be obtained. In this pattern, reinforcement is obtained about the peak originating in the {113} sides of alumina crystal system, and {030} sides. Generally, reinforcement is obtained as height of a peak. And obtained reinforcement I030 And I113 The rate of crystal orientation is called for according to formula I030/(I113+I030). In addition, generally, it is hexagonal and the crystal structure of a stable alumina of an a-axis and a b-axis is equivalent among three crystallographics axis as shown in drawing 4. Therefore, in the case of such hexagonal structure, the field (030) and the field (300) are equivalent, are named generically and made into {030} sides.

[0022] Drawing 5 shows typically signs that {030} sides carry out orientation to the front face, in the alumina-ceramics ingredient by this invention. The ingredient shown in drawing 5 has the configuration of a rectangular parallelepiped. Such an ingredient has one pair of principal planes (a top face and base), and the side face which exists between them. According to this invention, in such an ingredient, orientation of the {030} sides can be strongly carried out almost in parallel to one pair of principal planes (a top face and base), and the rate of crystal orientation mentioned above in these fields can be made or more into 0.34. These front faces whose rates of orientation are 0.34 or more have the more excellent plasma corrosion resistance, and have the engine performance which was excellent as a plasma exposure side. On the other hand, in such a case, {030} sides have not carried out orientation to a side face strongly. However, the side face in which the conditions of alumina purity, a sintered compact

consistency, and mean particle diameter are satisfied as mentioned above also has plasma corrosion resistance. The more excellent plasma corrosion resistance was able to be given by making the rate of crystal orientation on the front face of an ingredient or more into 0.34 so that the example shown below might show more concretely.

[0023] The front face which was excellent with such plasma corrosion resistance can be obtained in the manufacture process of the ceramics including shaping of powder and the process of sintering by carrying out temporary quenching of the alumina raw material powder at 1000 degrees C - 1150 degrees C, and carrying out pressing to 1 shaft orientations about the raw material which performed such temporary quenching treatment. According to a 1000 degrees C - 1150 degrees C [ such ] temporary-quenching process, alumina powder turns into raw material powder to which it has an anisotropy about a configuration, and particle size was equal (that is, the raw material with which neck growth took place is obtained). It is desirable to use the alumina powder of a high grade to which particle size was equal in what has comparatively small mean particle diameter (for example, mean particle diameter of 0.3-0.5 micrometers) for the raw material powder for presenting such a temporary-quenching process. Such alumina powder can be obtained as a commercial item. As mentioned above, after carrying out temporary quenching of the alumina powder, the orientation of the {030} sides can be made to carry out in the direction almost perpendicular to these 1 shaft orientations strongly by pressing into 1 shaft orientations. Here, the compression moulding technique to which a load is applied only in the direction parallel to one certain shaft as the pressing of 1 shaft orientations as shown in drawing 6 is meant. The rate of crystal orientation can use the field where the pressure was put on 1 shaft orientations in the Plastic solid acquired after these processes as 0.34 or more front faces. The alumina ceramics according to this invention can be manufactured by performing CIP shaping after such a press of 1 shaft orientations, and subsequently sintering. On the other hand, after the pressing of 1 shaft orientations, even if it sinters without performing CIP shaping, an ingredient with the high crystal stacking tendency on the front face of a sintered compact can be obtained.

[0024] Except surely performing the temporary-quenching process mentioned above and the pressing process of 1 shaft orientations, the manufacture approach by this invention can follow the usual conditions. That is, in a general process, as the alumina powder (generally powder of stable alpha mold (corundum structure) alumina) of a high grade was mentioned above, after carrying out temporary quenching, an organic binder, a dispersant, water, etc. are added to the raw material powder obtained, and a slurry is prepared. If needed, a spray dryer etc. is used, the obtained slurry is corned and dried, and the end of agglomerated powder is obtained. Thus, as the end of agglomerated powder it was obtained is put into metal mold and mentioned above, after carrying out pressing to 1 shaft orientations, CIP shaping is performed if needed. Thus, after heating the acquired Plastic solid and degreasing, sintering is performed and the alumina ceramics which have a required configuration according to an application are obtained. Sintering temperature can be made into 1550 degrees C - 1720 degrees C. Thus, about the obtained alumina-ceramics material, required processing of a grinding process, polish processing, etc. is performed, and a product is obtained through a suitable washing process etc. The obtained product can be offered as the component or components of the equipment used for a semi-conductor process which was mentioned above, for example.

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EXAMPLE

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[Example] Example mean particle diameter is 0.5 micrometers, while being 99.8% - 99.99%, temporary quenching of the alumina raw material powder which has various purity was carried out at 1000-1150 degrees C for 1 to 2 hours, and neck growth was made to perform. Thus, in the raw material powder 100 weight section which carried out temporary quenching, the water 60 weight section, the ammonium system dispersant 0.3 weight section, and the polyvinyl alcohol system binder 2 weight section were added, and the slurry was obtained by mixing with a ball mill for 16 hours. The agglomerated powder of spherical granulation was prepared by carrying out spray drying of the obtained slurry with a spray dryer. The obtained agglomerated powder is set to metal mold, and it is 300kg/cm<sup>2</sup> to 1 shaft orientations. Pressing was carried out by the pressure. To the acquired Plastic solid, it sets further at a rubber die, and is 2 1.2t/cm. CIP shaping was given by the pressure. It degreased by having carried out the temperature up of the acquired Plastic solid in the small electric furnace, it calcinated at 1550-1720 degrees C for 2 hours, and alumina ceramics were obtained. Thus, the front face of the obtained alumina ceramics was wrapped with the precision grinder, using a diamond slurry with a mean particle diameter of 0.5-1.0 micrometers as abrasives, and the member front face was mirror-plane-ized.

[0026] About the obtained alumina-ceramics ingredient, bulk density, alumina purity, the diameter of average crystal grain, the rate of crystal orientation, the etch rate by plasma exposure, and anti-chip box reinforcement were measured. Bulk density was measured by the Archimedes method. Alumina purity was measured by ICP emission spectrometry. The diameter of average crystal grain was measured by photo finish by SEM observation. a crystal -- orientation -- a rate -- measurement -- \*\*\*\* -- GONIO -- a formula -- X-ray diffractometer -- using -- each -- an alumina -- an ingredient (10mmx10mm) -- main -- a front face -- receiving -- an X diffraction -- an image -- observing -- an angle of diffraction -- whenever -- 43.36 -- degree -- 68.19 -- degree -- respectively -- appearing -- {-- 113 --} -- a field -- {-- 030 --} -- a field -- a peak -- diffraction -- reinforcement -- from -- a formula --  $I_{030} / (I_{113} + I_{030})$  -- the rate of crystal orientation -- having asked . In the plasma exposure to a ceramic ingredient, the plasma exposure was carried out on the conditions shown in Table 1 using parallel monotonous mold ion etching equipment. The mask on a Teflon tape was partially prepared in the exposure side (polished surface mentioned above) of each trial ingredient, and the plasma exposure was performed. The Teflon tape after an exposure was removed, and the amount of corrosion in a plasma exposure side (the amount of damages) was calculated on the basis of the non-irradiating field (plasma non-irradiated side) by which the mask was carried out, and it asked for the total etch rate. This amount of damages was calculated from both level difference measurement with the exposure side and the non-irradiating field by the sensing-pin type level difference meter, and measurement of the amount of surface irregularity by the atomic force microscope (AFM). That is, as shown in drawing 7 , the amount of surface irregularity shown by A was calculated by AFM, and the amount of level differences shown by B was calculated with the sensing-pin type level difference meter. The amount of damages by the plasma totals these amounts. Moreover, it asked for the anti-chip box reinforcement of each trial ingredient by the three-point bending test.

[0027]

[Table 1]

照射条件

高周波周波数	13.56 MHz
高周波出力	0.8 kW
電極間距離	~ 20 cm
エッチングガス種	CF <sub>4</sub>
雰囲気圧力	5 Pa
照射時間	3 時間

[0028] The example mean particle diameter of a comparison is 0.5 micrometers, while being 99.3% - 99.99%, about the examples 1-4 of a comparison, temporary quenching of the alumina raw material powder which has various purity was carried out at 1020-1210 degrees C for 1 to 2 hours, and neck growth was made to perform. Thus, in the raw material powder 100 weight section which carried out temporary quenching, the water 60 weight section, the ammonium system dispersant 0.3 weight section, and the polyvinyl alcohol system binder 2 weight section were added, and the slurry was obtained by mixing with a ball mill for 16 hours. The agglomerated powder of spherical granulation was prepared by carrying out spray drying of the obtained slurry with a spray dryer. the obtained agglomerated powder -- metal mold -- it is -- 1 shaft orientations -- 300kg/cm<sup>2</sup> Pressing was carried out by the pressure. It sets further to the acquired Plastic solid at a rubber die, and they are 1.2 t/cm<sup>2</sup>. CIP shaping was carried out by the pressure. After degreasing by carrying out the temperature up of the acquired Plastic solid using a small electric furnace, it calcinated at the temperature of 1510-1770 degrees C for 2 hours. After performing polish processing like [ alumina ceramics / which were obtained ] the above-mentioned example and mirror-plane-izing a front face, it asked for bulk density, purity, a mean diameter, the rate of crystal orientation, an etch rate, and anti-chip box reinforcement like the above-mentioned example.

[0029] Moreover, about the example 5 of a comparison, temporary quenching of the alumina raw material powder was not carried out, but, as for the pressing of 1 shaft orientations, agglomerated powder also performed CIP shaping, without carrying out. Other conditions were the examples 1-4 of a comparison, and these conditions.

[0030] The result obtained in the example and the example of a comparison, respectively is shown [ example / temperature / burning temperature and / temporary-quenching ] in Table 2 and 3 with burning temperature about the example of a comparison. It is the bulk density of alumina ceramics so that clearly [ compare these results and ] 3.94 g/cm<sup>3</sup> By making mean particle diameter to 4 micrometers - 15 micrometers, making alumina purity into 99.75% or more, and making the rate of crystal orientation of the front face or more into 0.34 shows above that the ingredient which is excellent in the corrosion resistance over the fluorine system plasma, and has high anti-chip box reinforcement is obtained. Moreover, in order to make the rate of crystal orientation on the front face of a sintered compact increase, a temporary-quenching process (neck growth process) is indispensable, and it turns out that the rate of crystal orientation on the front face of an ingredient increases with the rise of temporary-quenching temperature. In addition, in this invention, desirable temporary-quenching temperature is 1000-1150 degrees C, if this temporary-quenching temperature is less than 1000 degrees C, neck growth of alumina powder will not fully advance, and if temporary-quenching temperature exceeds 1150 degrees C, the diameter of granulation will become large, therefore pack density falls and the bulk density of the sintered compact obtained becomes small. In the alumina ceramic material by this invention, an etch rate is small in 0.5micrometers/[ an hour and ] or less so that clearly [ compare an ingredient (comparison material 1) with low bulk density, an ingredient with low purity (comparison material 2), an ingredient (comparison material 3) with a small particle size, an ingredient (comparison material 4) with a big particle size, and an ingredient with the low rate of crystal orientation (comparison material 5) with the ingredient obtained in the example and ], and anti-chip box reinforcement is



35kg/cm<sup>2</sup>. It turns out [ the above and ] that it is large. Moreover, signs that the ingredient of an example and the ingredient (comparison material 2) of the example of a comparison whose sintering temperature is 1670 degrees C were compared about the etch rate are shown in drawing 8 . With the ingredient by this invention, it is fewer than comparison material about all of the amount of etching by the level difference shown by the amount of etching and B by the irregularity shown by A, and it turns out that it has the corrosion resistance in which the ingredient by this invention was excellent to the fluorine system plasma so that clearly from drawing.

[0031]

[Table 2]

	焼成温度 (°C)	仮焼温度 (°C)	密度 (g/cm <sup>3</sup> )	純度 (%)	平均粒径 (μm)	結晶配向率	エッチング速度 (μm/hr)	抗析強度 (kg/mm <sup>2</sup> )
実施例	1550	1000	3.940	99.8	3.8	0.34	0.50	47
	1550	1150	3.942	99.8	4.8	0.36	0.47	43
	1610	1020	3.946	99.8	4.9	0.35	0.42	42
	1610	1110	3.948	99.8	4.7	0.37	0.40	45
	1630	1040	3.956	99.99	6.2	0.36	0.38	38
	1630	1150	3.954	99.99	6.8	0.39	0.33	40
	1650	1020	3.961	99.87	7.5	0.35	0.35	39
	1650	1100	3.963	99.87	7.2	0.38	0.33	40
	1650	1150	3.959	99.87	6.8	0.40	0.31	43
	1670	1100	3.964	99.91	8.2	0.38	0.35	35
	1670	1140	3.967	99.91	7.9	0.41	0.33	42
	1709	1040	3.969	99.85	12	0.41	0.32	33
	1709	1150	3.970	99.85	10	0.43	0.28	36
	1730	1030	3.975	99.99	14	0.41	0.2	32

[0032]

[Table 3]

		焼成温度 (℃)	仮焼温度 (℃)	密度 (g/cm <sup>3</sup> )	純度 (%)	平均粒径 (μm)	結晶配向率	エッチング速度 (μm/hr)	抗析強度 (kg/mm <sup>2</sup> )
比較例	1	1540	1210	3.915	99.92	4.2	0.35	0.87	43
		1550	1170	3.930	99.95	4.5	0.37	0.92	41
		1570	1180	3.935	99.8	4.6	0.37	0.80	46
	2	1650	1100	3.956	99.55	7.3	0.38	0.70	38
		1670	1080	3.962	99.3	8.5	0.37	1.20	32
	3	1510	1020	3.955	99.93	3.0	0.34	0.96	32
		1520	1050	3.950	99.92	3.2	0.35	0.88	39
	4	1750	1100	3.961	99.93	18	0.36	0.42	16
		1770	1120	3.971	99.99	21	0.39	0.39	12
	5	1630	—	3.956	99.99	7.2	0.28	0.78	38
		1650	—	3.961	99.87	7.6	0.29	0.65	41
		1670	—	3.964	99.91	10.2	0.31	0.55	40

[0033]

[Translation done.]

\* NOTICES \*

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing an example of plasma treatment equipment typically.

[Drawing 2] It is drawing showing the correlation of the crystal stacking tendency in the front face of an alumina-ceramics member, and the rate at which etching advances by the plasma on this front face.

[Drawing 3] It is the mimetic diagram showing the diffraction pattern obtained by X diffraction measurement.

[Drawing 4] It is the mimetic diagram showing the crystal structure of a stable alumina generally.

[Drawing 5] It is the mimetic diagram showing signs that the specific crystal face (specific crystal orientation) carries out orientation in a plasma exposure side in the alumina-ceramics ingredient by this invention.

[Drawing 6] It is a mimetic diagram for explaining the pressing of 1 shaft orientations.

[Drawing 7] It is the mimetic diagram showing signs that an alumina-ceramics ingredient is damaged by plasma exposure.

[Drawing 8] It is drawing which clarifies the difference between the ingredient by this invention, and the ingredient by the example of a comparison about an etch rate.

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[Translation done.]

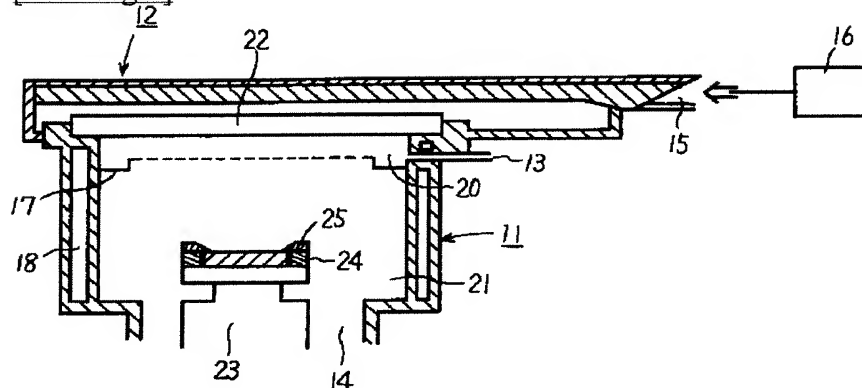
\* NOTICES \*

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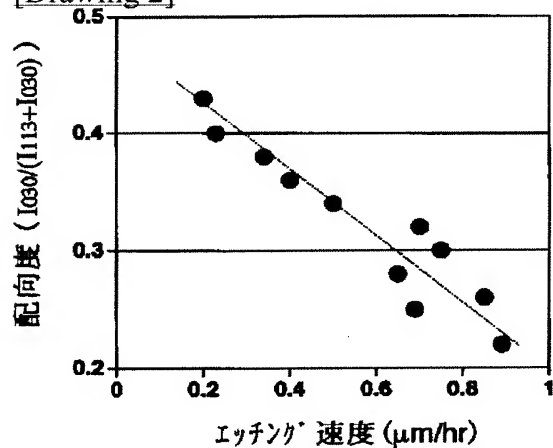
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3. In the drawings, any words are not translated.

## DRAWINGS

[Drawing 1]

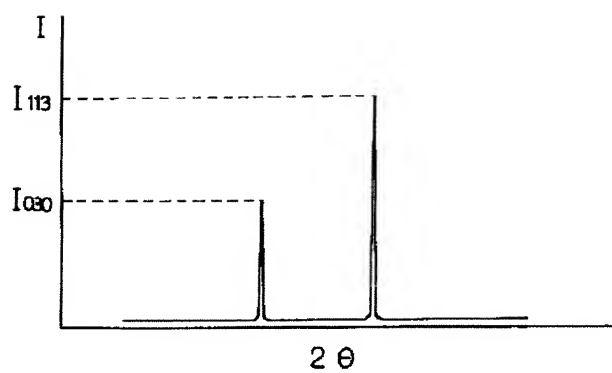


[Drawing 2]

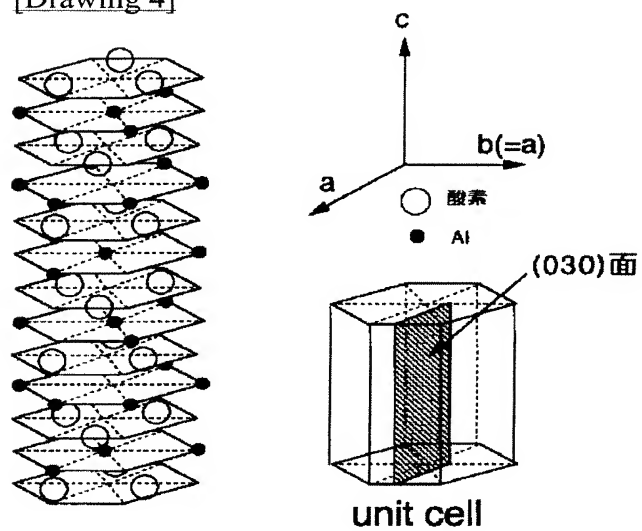


部材結晶配向性とエッチング速度との相関関係

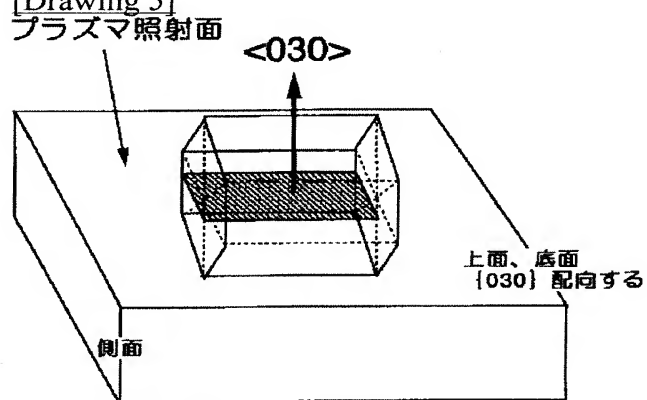
[Drawing 3]



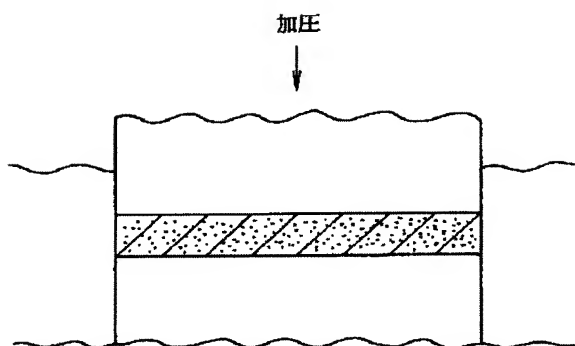
[Drawing 4]



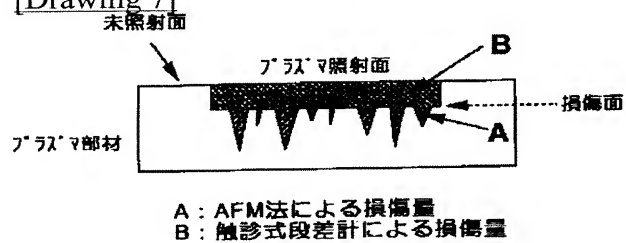
[Drawing 5]



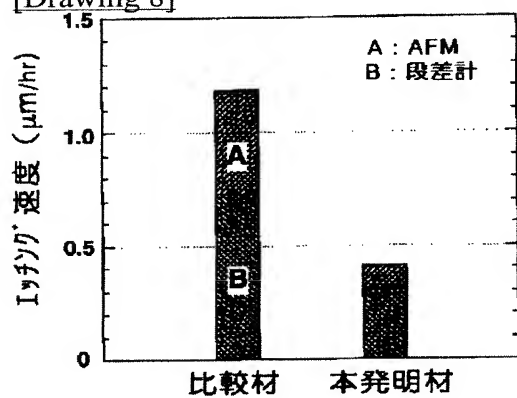
[Drawing 6]



[Drawing 7]



[Drawing 8]



各部材のエッチング速度  
焼成温度 : 1670°C

[Translation done.]

(19)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平11-310451

(43)公開日 平成11年(1999)11月9日

(51)IntCl <sup>5</sup>	識別記号	FI	
C04B 35/10		C04B 35/10	Z
H01L 21/205		H01L 21/205	
// H01L 21/3065		21/302	B

審査請求 未請求 請求項の数2 OL (全8頁)

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(54)【発明の名称】 プラズマ耐食性に優れたアルミナセラミックス材料およびその製造方法

(57)【要約】

【課題】 フッ素系プラズマに対して優れた耐食性を有するアルミナセラミックス材料を提供する。

【解決手段】 アルミナセラミックス材料は、アルミナ純度が99.75%以上であり、平均結晶粒径が4 $\mu$ m～15 $\mu$ mでありかつ嵩密度が3.94g/cm<sup>3</sup>以上であるアルミナ焼結体からなる。さらにアルミナセラミックス材料は、X線回折測定において式 $I_{030}/(I_{113} + I_{030})$  (式中、 $I_{030}$  および  $I_{113}$  はそれぞれX線回折測定により得られる回折パターンのアルミナ結晶(030)面および(113)面に対応するピークの強度である)によって求められる結晶配向率が0.34以上である表面をプラズマ耐食性の表面として有する。



## 【特許請求の範囲】

【請求項1】 アルミナ純度が99.75%以上であり、平均結晶粒径が $4\mu\text{m} \sim 15\mu\text{m}$ でありかつ嵩密度が $3.94\text{g}/\text{cm}^3$ 以上であるアルミナセラミックスからなり、かつX線回折測定において式 $I_{002}/(I_{002} + I_{113})$  (式中、 $I_{002}$  および  $I_{113}$  はそれぞれ前記X線回折測定により得られる回折パターンのアルミナ結晶(030)面および(113)面に対応するピークの強度である)によって求められる結晶配向率が0.34以上である表面をプラズマ耐食性の表面として有することを特徴とする、プラズマ耐食性に優れたアルミナセラミックス材料。

【請求項2】 アルミナ原料粉末を成形しかつ得られた成形体を焼結することによりアルミナセラミックス材料を製造する方法において、

前記アルミナ原料粉末を成形する前に、前記アルミナ原料粉末を $1000^\circ\text{C} \sim 1150^\circ\text{C}$ の温度で仮焼する工程と、

前記仮焼を施した材料について一軸方向に加圧成形を施す工程とを備えることを特徴とする、プラズマ耐食性に優れたアルミナセラミックス材料の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、プラズマ耐食性に優れたアルミナセラミックスおよびその製造方法に関し、特に、エッチング、半導体エピタキシャル成長膜の作製、LSI回路の製造などの半導体プロセスに必要なフッ素系プラズマ照射に対して優れた耐食性を有するアルミナセラミックス材料およびその製造方法に関する。

## 【0002】

【従来の技術】プラズマエッチング装置、プラズマアッシング装置、プラズマCVD装置等のプラズマを用いて処理を行なう装置は、低温で効率よく必要な処理を行なうことができ、処理の制御も比較的簡単であり、半導体基板等の材料にダメージを与えるおそれが少ないという点から、高集積半導体装置、液晶表示装置等の製造において欠くことができないものとなっている。

【0003】これらの装置では、真空近くに減圧した処理を行なうべき容器内に、反応ガスを導入し、高周波やマイクロ波を印加してガス放電を起こさせてプラズマを生成させる。図1は、この種のプラズマ処理装置の一例を模式的に示すものである。この装置において、たとえば、試料台23上に載置され、その周りを保護プレート24で囲まれ、かつクランプ25によって保持された材料の表面にプラズマ処理を施す場合、排気口14から排気を行なって反応容器11内を所定の真空度に設定した後、ガス供給管13からプラズマ生成室20内にCF<sub>4</sub>、C<sub>2</sub>F<sub>4</sub>、C<sub>3</sub>F<sub>4</sub>、Cl<sub>2</sub>、HBr、Ar、O<sub>2</sub>等の反応性ガスを供給する。装置の作動中、冷却水が冷却水流通室18に流され、反応容器11の周辺は冷却される。マイ

クロ波は、マイクロ波発振器16から導波管15を介して誘電体線路12に導入される。これにより誘電体線路12下方に電界が形成され、形成された電界がマイクロ波導入窓22を通過してプラズマ生成室20内に導入される。ガス供給管13から供給されたガスは、プラズマ生成室20内に導入され、マイクロ波の照射によりプラズマ化される。プラズマのうち電氣的に中性のラジカルが主にメッシュ状の仕切板17を通過して反応室21内に広がり、材料の表面に到達し、プラズマ処理が施される。またこのような装置において、プラズマ処理すべき材料を保持する治具として、静電チャック等が用いられる。

【0004】このようなプラズマ処理装置において、マイクロ波導入窓、保護プレート、クランプ、静電チャック等はプラズマに晒される。したがって、これらの部材は、プラズマに対して耐食性を有する必要がある。特に、フルオロカーボンおよび他のフッ素含有ガスより生成される反応性のより高いフッ素系プラズマに対し、優れた耐食性を有する部材が望まれている。

【0005】特開平8-81258号公報は、耐ドライエッチング性に優れたアルミナセラミックス焼結体を提供するための技術を開示する。同公報によれば、アルミナセラミックス焼結体は、99.2重量%以上99.9重量%以下の酸化アルミニウムと残部がアルミニウム以外の金属の酸化物からなり、そこにおいて平均粒子径は $0.5\mu\text{m}$ 以上 $1.5\mu\text{m}$ 以下であり、かつ密度は $3.88\text{g}/\text{cm}^3$ 以上 $3.97\text{g}/\text{cm}^3$ 以下である。また研削加工した該焼結体は、 $1000^\circ\text{C}$ 以上 $1550^\circ\text{C}$ 以下の温度で0.1時間以上6時間以下にわたり加熱処理されている。

【0006】特開平8-231266号公報は、フッ素プラズマによるエッチングに対して強い抵抗性を有する改良されたアルミニウムセラミックス材料を提供するための技術を開示する。同公報によれば、改良されたアルミナセラミックス材料は、99.5重量%~99.8重量%のアルミナと、0.5重量%~0.2重量%のシリカ、CaO、MgO等のバインダとからなり、かつ $15\mu\text{m} \sim 30\mu\text{m}$ を中心とする単一モードの粒径分布を有する。

【0007】特開平9-2864号公報もまた、フッ素プラズマに対して高い耐性を有するアルミナセラミックス材料を提供するための技術を開示する。同公報によれば、多結晶アルミナセラミックス材料は、99.3重量%~99.7重量%のアルミナと、0.7重量%~0.3重量%のバインダとからなる未焼結体を形成し、約 $1400^\circ\text{C} \sim 1700^\circ\text{C}$ の温度で約8~12時間焼結することにより製造される。このとき、多結晶アルミナセラミックス材料中の未焼結粒子の面積%は0.1面積%を超えない。

## 【0008】

【発明が解決しようとする課題】半導体プロセス等のための装置に用いられるアルミナセラミックス部材には、プラズマ、特にフッ素系プラズマに対して優れた耐食性を有することの他に、プラズマ照射により局所的に損傷が進まないこと、ウエハ等の加工物への汚染が無視できるレベルのものであること、材料強度が比較的大きいこと、適当な工数によって製造できること等の条件を満たすことが望まれている。特開平8-231266号公報に開示されるアルミナセラミックス材料では、アルミナ純度が比較的低く、またバインダとしてCa、Mg等の元素を含むため、ウエハへの汚染が無視できないレベルになる可能性が考えられる。また、この材料では、粒径密度が比較的大きいため、典型的な強度の目安が40,000psi(約28kg/mm<sup>2</sup>)と比較的小さい。また、このような材料は焼結体密度が比較的小さいため、プラズマ照射により局所的に損傷が進みやすい(深く掘れやすい)と考えられる。特開平9-2864号公報に開示されるセラミックス材料も、比較的アルミナ純度が低く、またバインダとしてCa、Mg等の元素を含むため、ウエハへの汚染が無視できないレベルになる可能性があると考えられる。また同公報に開示される製造プロセスは、工程数が比較的多く、焼結時間が8~12時間と比較的長いので、生産効率がそれほど良好なものではないと考えられる。特開平8-81258号公報に開示される技術では、焼結および研削加工の後に1000~1550℃で0.1~6時間の加熱処理が必要である。そのような加熱処理のために、焼結時に発生した歪み、マイクロクラック量等に応じて適正な条件を探索する必要があり、製造工程がより複雑になってくる。また、この技術では、具体的に示される焼結体密度がそれほど高くなっておらず、耐エッチング特性をさらに向上させるべき余地があると考えられる。

【0009】本発明の目的は、従来の材料よりもプラズマ照射に対する耐食性の優れたアルミナセラミックス材料を提供することである。

【0010】本発明のさらなる目的は、フッ素系プラズマに対する耐食性が優れかつ強度が高いアルミナセラミックス材料を比較的にシンプルなプロセスによって製造できる技術を提供することである。

【0011】

【課題を解決するための手段】本発明者は、アルミナ焼結体のフッ素プラズマに対する耐食性が、アルミナ純度、焼結体密度、平均粒径および結晶配向性に依存することを見だし、それらについてより好ましい条件を設定することにより、本発明を完成させるに至った。

【0012】すなわち、本発明によるプラズマ耐食性に優れたアルミナセラミックス材料は、アルミナ純度が99.75%以上であり、平均結晶粒径が4μm~15μmでありかつ嵩密度が3.94g/cm<sup>3</sup>以上であるアルミナセラミックスからなり、かつX線回折測定にお

て式 $I_{000} / (I_{111} + I_{000})$ (式中、 $I_{000}$  および  $I_{111}$  はそれぞれX線回折測定により得られる回折パターンのアルミナ結晶(030)面および{113}面に対応するピークの強度である)によって求められる結晶配向率が0.34以上である表面をプラズマ耐食性の表面として有することを特徴とする。

【0013】また本発明によるプラズマ耐食性に優れたアルミナセラミックス材料の製造方法は、アルミナ原料粉末を成形しかつ得られた成形体を焼結することによりセラミックス材料を製造する方法において、アルミナ原料粉末を成形する前にアルミナ原料粉末を1000℃~1150℃の温度で仮焼する工程と、仮焼を施した材料について一軸方向に加圧成形を施す工程とを備えることを特徴とする。

【0014】以上の特徴を有する本発明によれば、たとえば、プラズマ照射に対するエッチング速度が従来技術による部材よりも1/2以下に抑えられた部材を提供することができる。

【0015】

【発明の実施の形態】本発明は、たとえば、ウエハエッチング、アッシング、半導体エピタキシャル成長膜の作製、CVD、LSI回路製造、液晶表示装置製造などのプロセスに用いられる装置の構成要素または部品に適用することができる。より具体的には、本発明により、装置内壁材、シールド材、プレート材、クランプ材などの真空チャンバ部品、表面処理用ダミーウエハ、シリコンウエハ用ハンド、マイクロ波導入窓、静電チャックなどを構成することができる。以下、本発明をより具体的に説明する。

【0016】プラズマ照射によるセラミックス材の腐食は、結晶粒間の粒界と、結晶粒内とで進行する。セラミックス材料の耐食性を上げるためには、粒界に存在する耐食性の劣る不純物層の低減や空隙をなくすこと、結晶粒自体の耐食性を上げることの両方が重要である。

【0017】まず、アルミナセラミックスにおけるアルミナ純度を高めることで、焼結体中に含まれる不純物を減らし、粒界における不純物層の生成および析出を抑制することができる。本発明では、アルミナ純度を99.75%以上とすることによって、粒界でのプラズマによる腐食が少ない材料を提供する。この純度が99.75%を下回ると、より望ましい耐食性をセラミックス材料に付与することが困難になってくる。

【0018】また、成形体の嵩密度を上げる(緻密化する)ことで、粒界に存在する空隙部分を減少させることができ、プラズマに対する耐食性を向上させることができる。本発明では、セラミックス材料の嵩密度を3.94g/cm<sup>3</sup>以上とすることによって、プラズマ耐食性を向上させている。この嵩密度が3.94g/cm<sup>3</sup>を下回ると、より好ましい耐食性が得られなくなるほか、材料の強度も相対的に低くなる。

【0019】さらに、緻密化したアルミナ結晶粒の平均粒径を所定の範囲で大きくすることにより、プラズマ照射面に対してプラズマ抵抗性の低い（粒界）部分が占める割合（面積）を減らすことができる（すなわち粒界密度を減少させることができる）。本発明では、アルミナ結晶粒の平均粒径を4 μm以上15 μm以下としている。アルミナ結晶粒の平均粒径が増加すれば、粒界密度は減少するが、部材の抗折強度が次第に低下するため、その平均粒径は15 μm以下が好ましい。また、その平均粒径が4 μm未満の場合、粒界密度を十分に減少させることができず、粒界におけるプラズマ損傷の度合いが大きくなってくる。

【0020】さらに本発明者は、アルミナ結晶粒自体のプラズマによるエッチング量は、セラミックス材料におけるプラズマ照射面の結晶配向性に強く依存することを見いだした。そして、研究の結果、アルミナ結晶（h00）面および（0k0）面がセラミックス材料のプラズマ照射表面に多く分布しておれば、該表面は耐エッチング性に優れていることが判明した。図2は、そのような結果を具体的に裏付けるものであり、部材の結晶配向性とエッチング速度との相関関係を示している。図1において、縦軸はアルミナセラミックス材料の表面における結晶配向率（ $I_{h00} / (I_{h00} + I_{0k0})$ ）を示し、横軸は該表面がプラズマによりエッチングされる速度（μm/時間）を示す。図1より、結晶配向率が高くなればなるほどエッチング速度が低下する、すなわちプラズマによりエッチングされにくくなることが明らかである。これは、アルミナの各結晶面の中で（h00）面および（0k0）面がプラズマ照射に対して高耐食性であることを意味する。したがって、（h00）面および（0k0）面を、アルミナセラミックス材の表面に多く配向させることで、プラズマ耐食性を上げることが可能となる。

【0021】ここで、結晶配向率は、材料表面のX線回折測定により求められるものである。通常のX線回折装置を用い、材料表面を2θ/θ法（バルク材、粉末材料の結晶構造の同定に用いられる一般的な方法）によって測定すれば、たとえば図3に示すような回折パターンが得られる。このパターンにおいて、アルミナ結晶系の（113）面および（030）面に由来するピークについて強度を得る。一般に、ピークの高さとして強度が得られる。そして、得られた強度 $I_{h00}$ および $I_{0k0}$ より、式 $I_{h00} / (I_{h00} + I_{0k0})$ に従って結晶配向率が求められる。なお、一般に安定なアルミナの結晶構造は、図4に示すような六方晶であり、3つある結晶軸のうちa軸とb軸とは等価である。したがって、このような六方晶の構造の場合、（030）面と（300）面とは等価であり、総称して（030）面とする。

【0022】図5は、本発明によるアルミナセラミックス材料において、その表面に（030）面が配向する様

子を模式的に示している。図5に示す材料は、直方体の形状を有している。このような材料は、1対の主要面（上面および底面）とその間にある側面とを有する。本発明によれば、このような材料において、たとえば1対の主要面（上面および底面）に対してほぼ平行に（030）面を強く配向させ、これらの面において上述した結晶配向率を0.34以上とすることができる。配向率が0.34以上であるこれらの表面は、より優れたプラズマ耐食性を有し、プラズマ照射面として優れた性能を有する。一方、このような場合、側面には（030）面が強く配向していない。しかし、上述したようにアルミナ純度、焼結体密度および平均粒径の条件を満足する側面も、プラズマ耐食性を有するものである。以下に示す実施例によってより具体的に示すように、材料表面の結晶配向率を0.34以上とすることにより、より優れたプラズマ耐食性を付与することができた。

【0023】このようなプラズマ耐食性により優れた表面は、粉末の成形および焼結の工程を含むセラミックスの製造プロセスにおいて、アルミナ原料粉末を1000℃〜1150℃で仮焼し、そのような仮焼処理を施した原料について一軸方向に加圧成形することにより得ることができる。このような1000℃〜1150℃での仮焼工程により、アルミナ粉末は、形状について異方性を有しかつ粒径の揃った原料粉末となる（すなわちネック成長が起こった原料が得られる）。そのような仮焼工程に供するための原料粉末には、比較的平均粒子径が小さいもの（たとえば0.3〜0.5 μmの平均粒子径）で、粒径が揃った高純度のアルミナ粉末を用いることが望ましい。そのようなアルミナ粉末は、市販品として得ることができる。上述したように、アルミナ粉末を仮焼した後、一軸方向に圧縮成形することによって、この一軸方向にほぼ垂直な方向に（030）面を強く配向させることができる。ここで、一軸方向の加圧成形とは、たとえば図6に示すように、ある1つの軸に平行な方向にのみ荷重をかける加圧成形法を意味する。これらの工程の後、得られる成形体において一軸方向に圧力がかけられた面を結晶配向率が0.34以上の表面とすることができる。このような一軸方向のプレスの後、CIP成形を行ない、次いで焼結を施すことにより、本発明に従うアルミナセラミックスを製造することができる。一方、一軸方向の加圧成形の後、CIP成形を行わずに焼結を施しても、焼結体表面の結晶配向性が高い材料を得ることができる。

【0024】上述した仮焼工程および一軸方向の加圧成形工程を必ず行なうこと以外は、本発明による製造方法は通常の条件に従うことができる。すなわち、一般的なプロセスにおいて、高純度のアルミナ粉末（一般に安定なα型（コランダム構造）アルミナの粉末）を上述したように仮焼した後、得られる原料粉末に有機バインダ、分散剤、水等を添加してスラリーを調製する。得られたス

ラリを、必要に応じてスプレードライヤ等を用いて造粒、乾燥させて造粒粉末を得る。このようにして得られた造粒粉末をたとえば金型に入れて上述したように一軸方向に加圧成形した後、必要に応じてCIP成形を行なう。このようにして得られた成形体を、加熱して脱脂した後、焼結を行ない、用途に応じて必要な形状を有するアルミナセラミックスが得られる。焼結温度は、たとえば1550℃～1720℃とすることができる。このようにして得られたアルミナセラミックス材について、研削加工、研磨加工等の必要な加工を行ない、適当な洗浄工程等を経て製品が得られる。得られた製品は、たとえば上述したような半導体プロセスに用いられる装置の構成要素または部品として提供することができる。

#### 【0025】

##### 【実施例】実施例

平均粒子径が0.5μmであり、99.8%～99.99%の間で種々の純度を有するアルミナ原料粉末を1000～1150℃で1～2時間仮焼し、ネック成長を行なわせた。このようにして仮焼した原料粉末100重量部に、水60重量部、アンモニウム系分散剤0.3重量部およびポリビニルアルコール系バインダ2重量部を添加し、ボールミルで16時間混合することによりスラリーを得た。得られたスラリーをスプレードライヤで噴霧乾燥することにより、球状顆粒の造粒粉を調製した。得られた造粒粉を金型において一軸方向に300kg/cm<sup>2</sup>の圧力で加圧成形した。得られた成形体に、さらにゴム型において1.2t/cm<sup>2</sup>の圧力でCIP成形を施した。得られた成形体を小型電気炉において、昇温し、脱脂を行ない、1550～1720℃で2時間焼成してアルミナセラミックスを得た。このようにして得られたアルミナセラミックスの表面を、平均粒径0.5～1.0μmのダイヤモンドスラリーを研磨材として用い、精密研\*

##### 照射条件

高周波周波数	13.56 MHz
高周波出力	0.8 kW
電極間距離	～20 cm
エッチングガス種	CF <sub>4</sub>
雰囲気圧力	5 Pa
照射時間	3時間

#### 【0028】比較例

平均粒子径が0.5μmであり99.3%～99.99%の間で種々の純度を有するアルミナ原料粉末を比較例1～4については1020～1210℃で1～2時間仮焼し、ネック成長を行なわせた。このようにして仮焼した原料粉末100重量部に、水60重量部、アンモニウム系分散剤0.3重量部およびポリビニルアルコール系バインダ2重量部を添加し、ボールミルで16時間混合することによりスラリーを得た。得られたスラリーをスプレ

\* 磨損によりラッピングし、部材表面を鏡面化した。

【0026】得られたアルミナセラミックス材料について、嵩密度、アルミナ純度、平均結晶粒径、結晶配向率、プラズマ照射によるエッチング速度、および抗折強度を測定した。嵩密度は、アルキメデス法により測定した。アルミナ純度はICP発光分光法により測定した。平均結晶粒径は、SEM観察による写真判定により測定した。結晶配向率の測定には、ゴニオ式X線回折装置を用い、各アルミナ材料(10mm×10mm)の主表面に対するX線回折像を観測し、回折角度43.36°、68.19°にそれぞれ表われる{113}面、{030}面のピークの回折強度から式 $I_{113}/(I_{113}+I_{030})$ により結晶配向率を求めた。セラミックス材料へのプラズマ照射には、平行平板型イオンエッチング装置を用い、表1に示す条件でプラズマ照射を実施した。各試験材料の照射面(上述した研磨面)に部分的にテフロンテープによるマスクを設け、プラズマ照射を行なった。照射後テフロンテープを取り除き、マスクされていた非照射面(プラズマ未照射面)を基準としてプラズマ照射面における浸食量(損傷量)を求め、それからトータルのエッチング速度を求めた。この損傷量は、触針式段差計による照射面と非照射面との段差測定、および原子間力顕微鏡(AFM)による表面凹凸量の測定の両方から求めた。すなわち、図7に示すように、Aで示される表面凹凸量はAFMにより求められ、Bで示される段差量は触針式段差計によって求められた。プラズマによる損傷量は、これらの量をトータルしたものである。また、各試験材料の抗折強度は3点曲げ試験により求めた。

#### 【0027】

##### 【表1】

ードライヤで噴霧乾燥することにより球状顆粒の造粒粉を調製した。得られた造粒粉を金型において一軸方向に300kg/cm<sup>2</sup>の圧力で加圧成形した。得られた成形体にさらにゴム型において1.2t/cm<sup>2</sup>の圧力でCIP成形した。小型電気炉を用いて、得られた成形体を昇温し、脱脂を行なった後、1510～1770℃の温度で2時間焼成した。得られたアルミナセラミックスについて上記実施例と同様に研磨加工を行ない表面を鏡面化した後、上記実施例と同様に嵩密度、純度、平均粒

径、結晶配向率、エッチング速度および抗折強度を求めた。

【0029】また比較例5については、アルミナ原料粉末は仮焼せず、造粒粉も一軸方向の加圧成形は行わずにCIP成形を行なった。その他の条件は比較例1～4と同条件であった。

【0030】実施例および比較例においてそれぞれ得られた結果を、実施例については焼成温度および仮焼温度とともに、比較例については焼成温度とともに表2および表3に示す。これらの結果を比較して明らかなように、アルミナセラミックスの高密度を3.94g/cm<sup>3</sup>以上、平均粒径を4μm～15μm、アルミナ純度を99.75%以上とし、その表面の結晶配向率を0.34以上とすることにより、フッ素系プラズマに対する耐食性に優れかつ高い抗折強度を有する材料が得られることがわかる。また、焼結体表面の結晶配向率を増加させるには、仮焼工程（ネック成長過程）が必須であり、仮焼温度の上昇とともに材料表面の結晶配向率が増加することがわかる。なお、本発明において、好ましい仮焼温度は1000～1150℃であり、この仮焼温度が10×20

\*00℃を下回るとアルミナ粉末のネック成長が十分に進行せず、また仮焼温度が1150℃を超えると造粒径が大きくなり、したがって充填密度が下がり、得られる焼結体の嵩密度が小さくなる。嵩密度が低い材料（比較材1）、純度の低い材料（比較材2）、粒径が小さな材料（比較材3）、粒径が大きな材料（比較材4）および結晶配向率の低い材料（比較材5）と実施例で得られる材料とを比べて明らかなように、本発明によるアルミナセラミック材では、エッチング速度が0.5μm/時間以下と小さくかつ抗折強度が35kg/cm<sup>2</sup>以上と大きいことがわかる。また、焼結温度が1670℃である実施例の材料と比較例の材料（比較材2）とをエッチング速度について比較した様子を図8に示す。図から明らかなように、本発明による材料では、Aで示される凹凸によるエッチング量およびBで示される段差によるエッチング量のいずれについても比較材よりも少なく、本発明による材料がフッ素系プラズマに対して優れた耐食性を有することがわかる。

【0031】

【表2】

	焼成温度 (℃)	仮焼温度 (℃)	密度 (g/cm <sup>3</sup> )	純度 (%)	平均粒径 (μm)	結晶配向率	エッチング速度 (μm/hr)	抗折強度 (kg/mm <sup>2</sup> )
実施例	1550	1000	3.940	99.8	3.8	0.34	0.50	47
	1550	1150	3.942	99.8	4.8	0.38	0.47	43
	1810	1020	3.948	99.8	4.9	0.35	0.42	42
	1810	1110	3.948	99.8	4.7	0.37	0.40	45
	1830	1040	3.958	99.99	6.2	0.36	0.38	38
	1830	1150	3.954	99.99	8.8	0.39	0.33	40
	1850	1020	3.961	99.87	7.5	0.35	0.35	39
	1850	1100	3.963	99.87	7.2	0.38	0.33	40
	1850	1150	3.959	99.87	8.8	0.40	0.31	43
	1870	1100	3.964	99.91	8.2	0.38	0.35	35
	1870	1140	3.967	99.91	7.9	0.41	0.33	42
	1709	1040	3.969	99.85	12	0.41	0.32	33
	1709	1150	3.970	99.85	10	0.43	0.28	38
	1730	1030	3.975	99.99	14	0.41	0.2	32

【0032】

※ ※ 【表3】

		焼成温度 (℃)	仮焼温度 (℃)	密度 (g/cm <sup>3</sup> )	純度 (%)	平均粒径 (μm)	結晶配向率	エッチング速度 (μm/hr)	抗折強度 (kg/mm <sup>2</sup> )
比較例	1	1540	1210	3.915	99.92	4.2	0.35	0.87	43
		1550	1170	3.930	99.95	4.5	0.37	0.92	41
		1570	1180	3.935	99.8	4.6	0.37	0.80	48
	2	1650	1100	3.958	99.55	7.3	0.38	0.70	38
		1670	1080	3.982	99.3	8.5	0.37	1.20	32
	3	1510	1020	3.955	99.93	3.0	0.34	0.98	32
		1520	1050	3.950	99.92	3.2	0.35	0.88	39
	4	1750	1100	3.961	99.93	18	0.36	0.42	18
		1770	1120	3.971	99.99	21	0.39	0.39	12
	5	1630	—	3.956	99.99	7.2	0.26	0.78	38
		1650	—	3.961	99.87	7.6	0.29	0.65	41
		1670	—	3.984	99.91	10.2	0.31	0.55	40

【0033】

50 【発明の効果】以上説明してきたとおり、本発明によれ

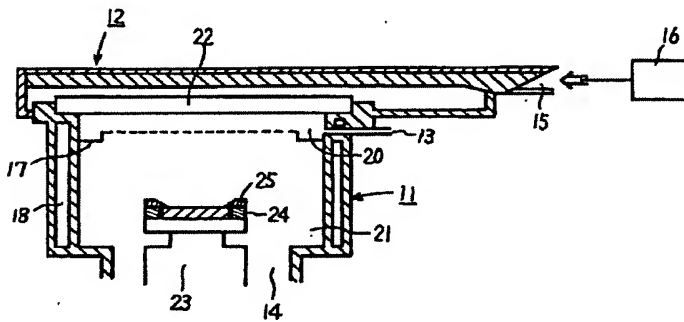
ば、プラズマ、特にフッ素系プラズマに対する耐食性がより優れ、かつ強度が高いアルミナセラミックス材料を得ることができる。本発明は、エッチング、アッシング、半導体エピタキシャル成長膜の形成、LSI回路の製造、液晶表示装置の製造など、半導体プロセスに用いられる装置の構成要素または部品として特に有用である。また、上述したように仮焼工程および一軸方向の加圧成形工程を組合せることによって、プラズマに対する耐食性のより優れた表面を有するアルミナセラミックス材料を得ることができる。このような製造方法は、特に

【図面の簡単な説明】

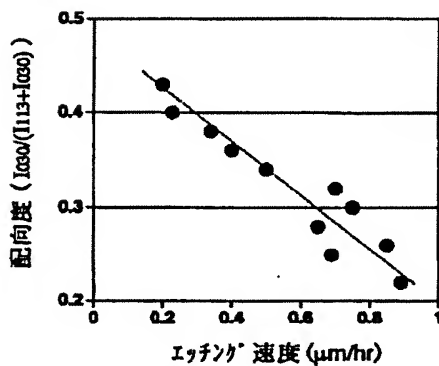
【図1】プラズマ処理装置の一例を模式的に示す断面図である。

【図2】アルミナセラミックス部材の表面における結晶\*

【図1】



【図2】



部材結晶配向性とエッチング速度との相関関係

\* 配向性と該表面でプラズマによりエッチングが進行する速度との相関関係を示す図である。

【図3】X線回折測定によって得られる回折パターンを示す模式図である。

【図4】一般的に安定なアルミナの結晶構造を示す模式図である。

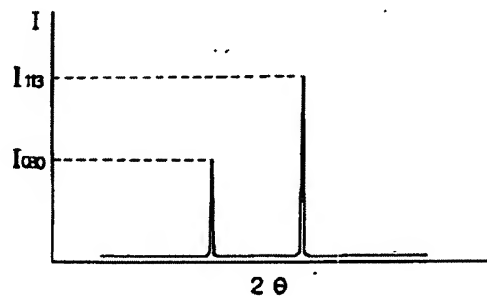
【図5】本発明によるアルミナセラミックス材料において特定の結晶面（特定の結晶方位）がプラズマ照射面において配向する様子を示す模式図である。

【図6】一軸方向の加圧成形を説明するための模式図である。

【図7】プラズマ照射によりアルミナセラミックス材料が損傷する様子を示す模式図である。

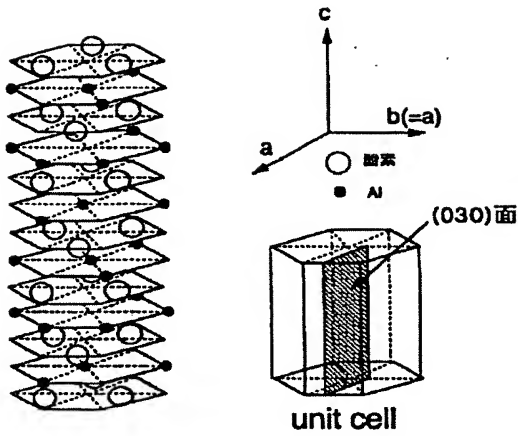
【図8】エッチング速度について、本発明による材料と比較例による材料との違いを明らかにする図である。

【図3】

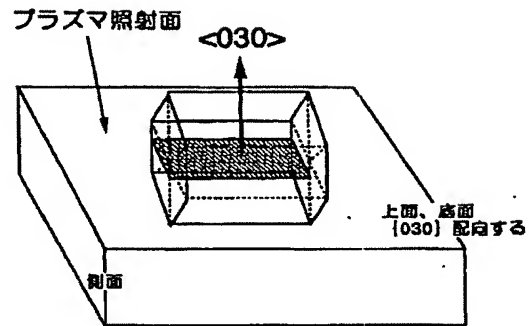




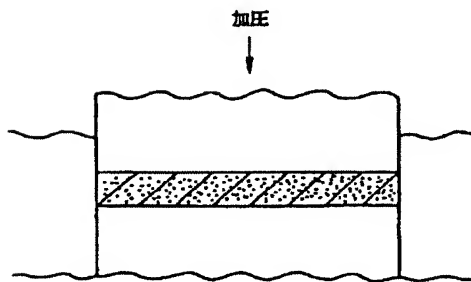
【図4】



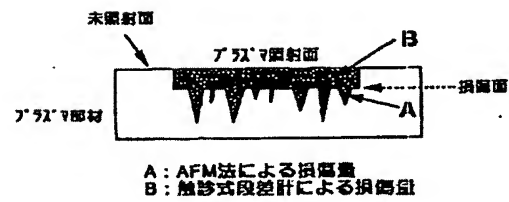
【図5】



【図6】



【図7】



【図8】

